Fabrication of lanthanum-doped thorium dioxide by high-energy ball milling and spark plasma sintering

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Abstract: High-energy ball milling was used to synthesize $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$ ($x = 0.09, 0.23$) solid solutions, as well as improve the sinterability of ThO_2 powders. Dense La-doped ThO_2 pellets with theoretical density above 94% were consolidated by spark plasma sintering at temperatures above 1400 °C for 20 mins, and the densification behavior and the non-equilibrium effects on phase and structure were investigated. A lattice contraction of the SPS-densified pellets occurred with increasing ball milling duration, and a secondary phase with increased La-content was observed in La-doped pellets. A dependence on the La-content and sintering duration for the onset of localized phase segregation has been proposed. The effects of high-energy ball milling, La-content, and phase formation on the thermal diffusivity were also studied for La-doped ThO_2 pellets by laser flash measurement. Increasing La-content and high energy ball milling time decreases thermal diffusivity; while the sintering peak temperature and holding time beyond 1600 °C dramatically altered the temperature dependence of the thermal diffusivity beyond 600 °C.

1. Introduction:

Thorium has drawn the attention of the nuclear community due to the potential implications of thorium fuel cycle, particularly on potentially-improved operational safety and non-proliferation. The thorium fuel cycle is based upon the fertile nature of Th^{232} , the sole isotope existing in a significant quantity in nature, and its transmutation to fissile U^{233} . The major benefits of the thorium fuel cycle are derived from the material properties of thorium, including the high melting point of ThO_2 (3,390 °C) as compared to that of uranium dioxide (2,865 °C), as well as increased thermal conductivity in ThO_2 over UO_2 and its lower thermal expansion [1, 2]. The oxidation behavior of thorium as a 4+ oxidation state as compared to uranium's 4+, 5+, and 6+ oxidation states benefits the fabrication and chemical stability of the fuel. The attractiveness of the thorium fuel cycle is further enhanced by the relative abundance of thorium as compared to uranium, with thorium being three to four times as common globally [1, 2]. The thorium fuel cycle has drawn attention for being proliferation resistant due to difficulties in the acid dissolution of ThO_2 as a result of the aforementioned chemical stability, and the high content of gamma-emitting U^{232} present in spent ThO_2 fuels [1-4]. However, drawbacks associated with the thorium fuel cycle, such as the necessity of reprocessing to fully utilize the benefits of the fuel cycle, and difficulties with such reprocessing due to the aforementioned chemical stability and high gamma-emissions, have resulted in a delayed implementation of thorium technologies.

While the majority of work pertaining to ThO_2 mixtures has focused on the combination of ThO_2 and major actinides in mixed oxide (MOX) fuels [5-8], the incorporation of lanthanides into the ThO_2 matrix has been an ongoing research topic for the nuclear community. Incorporation of lanthanides into ThO_2 has been previously researched with the goal of improving the performance of the ThO_2 -lanthanide systems for applications primarily related to

nuclear fuels. Prior investigations have focused on the effects of lanthanide dopants on the chemical stability [9], thermal conductivity [10, 11], thermal expansion [12], lattice parameter [13], and densification [14] of ThO₂-lanthanide systems.

In this study, the incorporation of the lanthanide into the ThO₂ systems was achieved by a low temperature solid-state reaction by high energy ball milling (HEBM). HEBM is a room temperature solid-state synthesis technique which allows for the simultaneous reduction of particle size and facilitation of phase transformations and/or incorporation of additives. HEBM has been previously utilized for the synthesis of nuclear fuels [15], photocatalysts [16], fuel cells [17], and nuclear waste forms [18]. HEBM was used in this study as the primary means of incorporating dopants into the ThO₂ matrix, and the additional effect of mechanically reducing the particle size allowed for a simple variation in starting particle sizes.

The dense La-doped ThO₂ pellets were consolidated by spark plasma sintering (SPS). SPS is a field-assisted sintering technique (FAST) which enables the reduction in the temperature and hold times required for densification; this creates the potential to fabricate fully-densified ceramics with significant reductions of energy cost as compared to conventional techniques [19, 20]. SPS, as a rapid consolidation technology, has attracted extensive attention in nuclear communities for fabricating advanced nuclear fuels. For example, SPS has been utilized in sintering high-density ThO₂ [21], UO₂ [22], and CeO₂ [23].

This work outlines the procedure to synthesize nano-sized ThO₂ powders, both with and without incorporating lanthanum oxide, through HEBM as well as the sintering routine to produce fully densified ThO₂ and Th_{1-x}La_xO_{2-0.5x} pellets via SPS. SPS was used to not only densify the ThO₂ and Th_{1-x}La_xO_{2-0.5x} powders, but investigate the effect of non-equilibrium conditions during sintering of doped samples. The effects of the dopant content, milling time,

and sintering parameters on ThO₂ sinterability and pellet densification were investigated. The structure and phase evolution including the phase formation and the secondary phase segregation due to non-equilibrium conditions during synthesis and sintering, and their effects on thermal-physics properties were also investigated.

2. Experimental details

2.1 La incorporation and ThO₂ powder fabrication

Nano-sized powders of La-doped ThO₂ were fabricated via HEBM (Fritsch, Pulverisette 7 Premium Line, Idar-Oberstein, Germany). Thorium dioxide (99.9% purity; International Bio-Analytical Industries Inc.) and lanthanum oxide (99.99% purity; Acros Organics) powders were used without further purification. Powders were mixed at weight ratios corresponding to the desired atomic ratios, and 10 g of mixture was loaded into the milling jars in 10 mL of ethanol. HEBM was carried out using a zirconia bowl (80 ml) and balls (1.5 mm diameter) for 12 h to 18 h milling time at 600 rpm, with a milling pattern of 15 minutes on, 5 minutes off, to prevent overheating of the ball mill, until the mixture was determined to be homogeneously blended by x-ray powder diffraction.

2.2 Spark plasma sintering

Spark plasma sintering was carried out using a Dr. Sinter ® SPS-211 Lx system with a procedure similar to our previous work. [15] To prepare each sample, approximately 1 g of powder was loaded into a graphite die, 10 mm in diameter. Graphite paper (0.20 mm thick) was used to envelope the powders, ensuring proper fit during assembly, ease of sample retrieval after sintering, and sufficient contact to facilitate the current passing through the assembly. The die was then wrapped in a graphite felt to insulate the die from radiative heat loss during fabrication.

The fully assembled graphite die was then arranged between graphite spacers, and loaded into the SPS between the rams of the hydraulic press with an applied pressure of 10 MPa.

Sintering was conducted under flowing argon, with current applied in a 25 ms on, 3 ms off pulse pattern. The sample temperature, which was measured using a pyrometer, was gradually increased from 25 °C to 600 °C before being increased to the peak temperature (between 1300 °C and 1700 °C) at a rate of 100 °C/min (Fig. 1). The uniaxial pressure applied by the hydraulic press was increased to 40 MPa at a rate which allowed it to reach its maximum value simultaneously with the temperature. The peak temperature was held at for a set period of time, (5 minutes unless otherwise noted) and then cooled to 100 °C below the peak temperature at a rate of 20 °C/min. The applied pressure was reduced during this cooling to 10 MPa at a rate of 6 MPa/min. The sample was then held at this reduced temperature for another 5 minutes, before being allowed to cool freely under the flowing argon.

2.3 Characterization

Density measurements were carried out using the Archimedes' method, by immersing the samples in deionized water using an Adam analytical scale (Danbury, NY, USA). X-ray diffraction measurements were carried out using a Panalytical X'Pert Pro system (Westborough, MA, USA) with a copper target ($K_{\alpha} = 0.15406$ nm) and a step size of 0.0131° . Scanning electron microscopy (SEM) as well as energy dispersive spectroscopy (EDS) measurements were conducted using a Zeiss 1540XB CrossBeam (Jena, Germany). SEM was also conducted on a Carl Zeiss Supra (Jena, Germany). In order to reduce charging during SEM, samples were coated in a thin layer of platinum under an argon environment via a Denton Sputter system (Denton Vacuum, LLC, NJ, USA). Thermal diffusivity measurements were taken using laser flash analysis (LFA-457, NETZCH, Germany), and the samples were coated with a thin layer of

graphite in order to promote photon absorption and consistency. Measurements were taken in an argon environment with a flow rate of 150 ml/min. Sample density was corrected to 100% theoretical density in order to correct for density variation between samples of identical compositions.

3. Results and discussion

X-ray powder diffraction of the HEBM mixture of ThO_2 and La_2O_3 indicates that the incorporation of La_2O_3 into the ThO_2 matrix occurs, with the patterns matching that of ThO_2 , with no observable residue peaks and minor peak shifting identified from pure ThO_2 without ball milling (Fig. 2). This agrees with prior studies regarding the ThO_2 - La_2O_3 system, which demonstrated the formation of a solid solution, with La solubility up to 50 mol.% *via* co-precipitation [14]. Minor lattice parameter changes were observed among the powders, with 12h HEBM resulting in a minor (0.0001 nm) decrease in lattice parameter and La-contents of 0.09 and 0.23 resulted in increases of 0.0003 nm and 0.0008 nm, respectively, as compared to ThO_2 undergoing similar HEBM. The trend of increasing lattice parameter with La incorporation agrees with prior research, as the ion size mismatch between Th^{+4} (0.105 nm) and La^{+3} (0.116 nm) should result in an expanded lattice with the replacement of Th with La. However, the magnitude of lattice expansion is reduced from prior experiments, suggesting that lattice contractions from HEBM play a competing role. Morphological measurements by SEM images display micron-sized agglomerates, a typical feature of high energy ball. Bright-field TEM images (Fig. 3) show ultrafine nanoparticles with the agglomerates with the particle size in the range of 10-20 nm for both ThO_2 and La-doped ThO_2 upon HEBM, significantly improving the sinterability of the ball milled powders as compared with pristine micro-sized powders.

SPS densification of ThO₂ powders (Fig. 4A) indicates an improvement in sinterability with increasing mill time, with a general trend of density increasing with peak sintering temperature and then saturating as density approached the theoretical maximum. The enhancement of sinterability is exemplified by the 300 °C reduction in peak sintering temperature required to achieve full densification ($\geq 95\%$ T.D.) between the as-purchased ThO₂ and the 18h HEBMed-ThO₂. This improvement in sinterability may be attributed to increasing particle surface area with milling time. Similar behavior has been previously reported in literature, with the reduction in starting ThO₂ particle size reducing the temperature threshold for the onset of sintering, resulting in increased density under identical sintering conditions [21].

SPS densification of Th_{1-x}La_xO_{2-0.5x} powders (Fig. 4B) resulted in a similar trend between density and peak sintering temperature, with density increasing with temperature. However, the La-doped powders were noticeably less densified under similar conditions, even after correcting for the lower theoretical density. The La-doped powder displayed sintering properties closer to those of the as-purchased ThO₂, as compared to the powders processed using HEBM, despite having been synthesized *via* 12h of HEBM. This is not consistent with the expectation in which the incorporation of La into the ThO₂ system increases the concentration of the oxygen vacancies, promoting atomic diffusion and thus sintering processing. This reduction in sinterability for La-doped ThO₂ may be due to the structural distortion upon La incorporation.

SEM images (Fig. 5) indicate that increased milling time resulted in minor reductions in grain sizes of ThO₂ pellets, with samples sintered at 1600 °C and undergoing HEBM for 12h and 18h displayed grain sizes of $3.2 \pm 0.6 \mu\text{m}$ and $2.9 \pm 1.1 \mu\text{m}$, respectively. This is consistent with the grain refinement of the starting materials for sintering by elongated ball milling. SEM images (Figs. 5C and 5D) further suggest La-incorporation into ThO₂ reduces grain growth during

sintering, with $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ and $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ pellets sintered at 1600 °C displayed grain sizes of $1.4 \pm 0.4 \mu\text{m}$ and $1.0 \pm 0.2 \mu\text{m}$, respectively. This reduction in grain size is presumably due to a reduction in atomic diffusion during sintering due to La-incorporation combined with a pinning of the grain boundaries by La-rich phases. Little-to-no grain coarsening was observed in La-doped samples when held at peak temperature during sintering for an hour, with $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ pellets sintered at 1600 °C for 1 hour displayed grain sizes of $1.5 \pm 0.3 \mu\text{m}$. This was an unexpected phenomenon and may associated with the aforementioned reductions in grain sizes observed with La-incorporation as compared to pure ThO_2 pellets. SEM images further displayed the low porosity of the sintered pellets, reinforcing the high degree of densification measured using Archimedes' method.

XRD results (Fig. 6 and 7) of HEBM- ThO_2 and La-doped ThO_2 samples sintered at different temperatures by SPS clearly show lattice contraction upon HEBM and lattice expansion with the incorporation of La_2O_3 as evidenced by the XRD diffraction peak shifting. The decrease in lattice parameter due to HEBM of the starting powders is readily apparent by comparing the sintered ThO_2 samples (Fig. 7A). HEBM resulted in a reduction of approximately 0.0015 nm for the densified pellets, with minor differences between 12 h and 18 h milling times. The minor changes in lattice parameter between milling times, coupled with the increased sinterability further supports the idea that the lattice parameter changes are due to a plastic deformation and strain induced on the lattice during HEBM; while the enhancement to sinterability may be associated with reductions in particle size.

XRD peak positions and lattice parameters prior to 1600 °C peak sintering temperature display slight changes from ThO_2 undergoing identical HEBM and SPS, with $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ and $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ displaying 0.0002 nm and 0.0009 nm increase in lattice parameter from

12h HEBM ThO₂ at 1500 °C, respectively (Fig. 8). The lattice expansion upon La incorporation is due to the difference in ion size between Th⁺⁴ (0.105 nm) and La⁺³ (0.116 nm) [24]. The resulting structural distortion observed from the incorporation of La into the ThO₂ matrix [11] is consistent with previous results of reducing sintering in Y₂O₃-doped CeO₂ with increasing dopant concentration [25].

A minor peak associated with La₂O₃ was observed at 1600 °C in Th_{0.91}La_{0.09}O_{1.955} and at and beyond 1600 °C in Th_{0.77}La_{0.23}O_{1.885}. The existence of the minor La₂O₃ phase may be caused by an incomplete incorporation of La₂O₃ into ThO₂ at room temperature by HEBM and rapid consolidation of SPS at temperature below 1600 °C. The unreacted La₂O₃ becomes increasingly more crystalline as temperature increases and observable *via* XRD. The other possibility might be localized incorporation of La₂O₃ into ThO₂ above its solubility limit during HEBM and the gradual segregation upon SPS sintering. However, the solubility of La reaches to x=0.50 for La_xTh_{1-x}O_{2-0.5x} prepared by a co-precipitation approach. A decrease in La₂O₃ solubility was reported when incorporated using solid-state reactions, with a maximum solubility observed for a La-content of x=0.30, as compared to formation using techniques such as co-precipitation [11]. No potential explanation was offered as to the solubility decrement between solid-state reactions and co-precipitation. Therefore, it is unlikely that the emergence of the minor phase La₂O₃ was caused by localized incorporation above its solubility in ThO₂ for Th_{0.91}La_{0.09}O_{1.955} since the incorporation amount is significantly less than the solubility observed for solid-state reaction. Because the Th_{0.91}La_{0.09}O_{1.955} samples sintered at 1700 °C or elongated sintering at 1600 °C for 1 h did not present La₂O₃, it implies that La₂O₃ may not be completely incorporated into ThO₂ upon HEBM at room temperature and rapid consolidation of SPS at lower sintering temperature. At 1600 °C, unincorporated and pre-damaged La₂O₃ by HEBM displays increased crystallinity,

responsible for the observation of the minor phase in XRD. Unreacted La_2O_3 was completely incorporated into the ThO_2 matrix with the increase of sintering temperature and elongated sintering time approaching to equilibrium conditions. For $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$, due to the higher amount of La incorporation, the minor phase still existed for SPS densified pellets at 1700 °C and 1600 °C for 1 h.

A temperature dependent phase evolution also occurs at and above 1600 °C during SPS. Based on the peak positions (Fig. 7), major phases present at 1600 °C in La-doped samples appear to correspond with La-doped ThO_2 of varying La content, La-rich at lower angle, and La-deficient at higher angle, along with the emergence of minor peaks associated with La_2O_3 . The emergence of the lower angle peak, associated with a La-doped ThO_2 phase of higher content (La-rich), as well as minor peaks associated with La_2O_3 with increasing sintering temperature is readily observed through the change in $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ samples (Fig. 8B). At 1500 °C, XRD indicates a single phase, matching the pattern of ThO_2 , with a 0.0009 nm increase in lattice parameter compared to samples prepared via 12h HEBM. This minor change is a result of the competition between lattice contraction due to HEBM and the lattice expansion from La incorporation. At 1600 °C, the intensity of the ThO_2 peak is dramatically reduced, along with the emergence of the La-rich phase, accompanied by minor peaks indicating La_2O_3 . At 1700 °C, the peaks associated with the La-deficient phase are completely eliminated, replaced by the La-rich phase and the minor La_2O_3 peaks. This is consistent with the previous analysis that La_2O_3 was not completely incorporated into ThO_2 matrix during HEBM at room temperature and SPS rapid sintering at lower temperatures, leading to a dominant La-deficient ThO_2 phases due to the non-equilibrium conditions of SPS. At higher sintering temperature and elongated sintering duration,

the unreacted La_2O_3 was gradually incorporated into the La-deficient phase, transforming to the La-enriched phase.

The non-equilibrium effects of HEBM and SPS were thought to contribute to the observed phase evolution phenomenon; in order to test this, the SPS routine was modified, extending the holding time of the peak temperature from 5 mins to 1h. This was carried out for both the investigated La contents at 1600 °C. The resulting XRD patterns indicated diverging results based on La-content (Fig. 7). The $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ sample produced a pattern closely resembling that of the 1500 °C and 1700 °C samples, with a singular phase similar to the 12h HEBM ThO_2 . The $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ sample produced a similar pattern to the associated 1600 °C sample, with minor La_2O_3 peaks present, along with a diminished ThO_2 peak and more intense La-doped ThO_2 peaks. This suggests that the non-equilibrium effects of SPS may play a role in the observed phase evolution; however the dopant content significantly impacts the degree of reincorporation into the strained ThO_2 matrix, as the availability of La changes throughout the material. This may be supported by the previously discussed decrease in La_2O_3 solubility when incorporated into ThO_2 via solid-state reactions [11].

The calculated lattice parameters of the La-rich phases based on lattice parameter changes from prior studies [9, 13], when corrected for the lattice contraction induced via HEBM, correspond to a La content of $x \approx 0.27$ for $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ and $x \approx 0.33$ for $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$, near the solubility limit experimentally determined for solid-state reactions. The La-content of the La-rich phase corresponding to the solubility limit, along with the presence of minor La_2O_3 peaks suggest that during the non-equilibria sintering conditions of SPS, non-uniform and localized incorporation of La_2O_3 in ThO_2 occurs, leaving some unreacted La_2O_3 in the ThO_2 - La_2O_3 mixture. This resulted in a La-deficient phase closely resembling ThO_2 for the pellets sintered

below 1600 °C and a La-enriched ThO₂ and excess La₂O₃ at 1600 °C. Upon sufficient sintering temperature or duration, as observed in the Th_{0.91}La_{0.09}O_{1.955} samples sintered at 1700 °C and 1600 °C for 1 hour, the incorporation of La₂O₃ becomes more uniform, leading to the elimination of minor La₂O₃ and the La-rich phase and a singular La-doped phases corresponding to the designed composition of Th_{0.91}La_{0.09}O_{1.955}. On the other hand, for the Th_{0.77}La_{0.23}O_{1.885} samples, due to the higher La content, limited incorporation of La into ThO₂ occurs at 1500 °C, but the La-deficient peaks were eliminated in the samples sintered at 1700 °C, suggesting the increased temperature enabled the incorporation of La to the solubility limit for solid-state reaction in ThO₂-La₂O₃.

The phase decomposition and elemental partitioning into La-rich and La-depleted ThO₂ phases were further confirmed by SEM images and energy dispersive spectroscopy (EDS). Backscattered electron images of the Th_{0.77}La_{0.23}O_{1.885} sample sintered at 1600 °C (Fig. 9A) indicate the presence of a secondary phase of lower atomic mass at the sub-micron scale, distributed bimodally between nano-metered (less than 50 nm) and sub-micron (200-500 nm) sizes. This darker secondary phase was confirmed *via* EDS (Figs. 9B, 9C) to be a La-rich phase with the surrounding lighter phase displaying La-deficiency. The confirmation of the La-rich secondary phase occurring at the sub-micron scale reinforces the idea that localized phase segregation occurred due to the sintering conditions and La-incorporation.

Thermal diffusivity measurements indicate a strong decrease in diffusivity among ThO₂ samples prepared using HEBM (Fig. 10A), with increasing mill time resulting in a minor degradation of diffusivity. This is most likely a result of an increase in the number of grain boundaries due to reduced grain size; because the grain boundaries act as phonon scattering sites, this results in a decreased thermal diffusivity in the samples prepared using HEBM. This

dependence of thermal performance on grain size has been previously observed in yttria-stabilized zirconia [26].

La_2O_3 incorporation into ThO_2 dramatically decreased the thermal diffusivity of samples, beyond the decrease associated with HEBM processing (Figs. 10B, 10C), with increasing La content resulting in a further decrease in thermal diffusivity. This reduction in thermal diffusivity was expected, and agrees with prior studies on the thermal effects of La doping on ThO_2 [10, 11, 13]. The general trend of thermal diffusivity for La-doped samples at lower SPS temperatures ($\leq 1600^\circ\text{C}$) was a gradual decrease of thermal diffusivity with temperature until approximately 600°C , followed by a gradual increase in diffusivity as temperature increased, with the diffusivity at 1000°C nearly reaching the room temperature diffusivity of the sample. The diffusivity reduction in the La-doped samples as compared to ThO_2 with identical HEBM processing is considerably less pronounced at higher temperatures, and may be further reduced at temperatures above 1000°C based on the observed trends. La-doped samples sintered above 1600°C and those allowed to reach equilibrium during sintering (held at peak temperature for 1 hour), displayed different thermal diffusivity trends than identically processed samples that underwent the standard 5 minutes hold at peak SPS temperature at or below 1600°C (Figs. 10B, 10C). These samples exhibited a similar trend to pure ThO_2 , a steady decrease in thermal diffusivity with temperature while still displaying the reduction in diffusivity associated with La doping.

A transition from photon-dominated heat transport to electron-dominate transport occurred in UO_2 , leading to the increase of thermal conductivity above 1500°C . However, similar to UO_2 , ThO_2 is a wide band gap material, and electron contribution may not dominate thermal transport above 600°C . This change in the temperature dependence of the thermal diffusivity may be

attributed to competition between phase/microstructure evolution and strain relaxation of the samples upon different sintering or measurement conditions that impact the phonon transport and interaction behavior. Specifically, the defect resistivity increases as a result of micro-strain and defect accumulation and heteroatom scattering upon the large sized La^{3+} incorporation into Th^{4+} sub-lattices and creation of oxygen vacancies[10]. The existence of the La-enriched and Th-enriched dual phases in the La-incorporated samples upon rapid SPS consolidation also increases the defect thermal resistivity due to interfacial and boundary scattering. The increased thermal diffusivity occurred above 600 °C for the La-incorporated samples maybe attributed to strain relaxation upon higher temperature annealing. In addition, nano-sized secondary phase may be incorporated into the Th-enriched phase during laser flash measurement, reducing the interfacial resistivity. On the other hand, higher temperature sintering (1700 °C) and/or prolonged holding time (1 hr) at peak sintering temperature allow more uniform incorporation of La in the ThO_2 phases and thus dominate phonon scattering resulting from heterogeneous atom doping. This may result in thermal behavior similar to that of pure ThO_2 samples, in which the phonon scattering dominates the thermal transport at measurement temperatures up to 1000 °C, but with the thermal diffusivity penalty expected for La_2O_3 incorporation.

4. Conclusions

High-energy ball milling was shown to improve sinterability in ThO_2 powders while being a suitable method for the incorporation of La_2O_3 into ThO_2 . Spark plasma sintering densification was used to achieve high-density pellets of ThO_2 and $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$. A complete incorporation of lanthanum was not achieved by solid state reaction at room temperature by HEBM. Temperature dependent phase segregation of La_2O_3 and La-rich and La-deficient $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$ was observed *via* X-ray diffraction, and supported by thermal diffusivity measurements. The

non-equilibrium conditions of SPS were shown to affect phase segregation based on the dopant content, with the lower dopant content maintaining a single phase, and the higher content displaying the phase segregation, potentially due to the previously observed decrease in La_2O_3 solubility associated with the solid-state reaction synthesis of $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$. The phase behavior of the La-doped ThO_2 is correlated with the amount of La doping and incorporation of lanthanum into ThO_2 affected by SPS temperature and duration. La_2O_3 incorporation into ThO_2 was shown to dramatically reduce thermal diffusivity, with the studied non-equilibria effects and associated phase segregation demonstrably altering the temperature dependence of thermal diffusivity.

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Graphical Abstract:

Highlights:

- Lanthanum incorporation into ThO₂ by high energy ball milling and rapid

consolidation of densified pellets by spark plasma sintering

- Elucidation of phase behavior of the La-doped ThO₂ and their correlation with the amount of La doping, incorporation of La and SPS sintering temperature/duration
- Investigation of the effects of La incorporation and high energy ball milling on the thermal transport behavior of the La-doped ThO₂.

Figures:

Fig. 1

Typical spark plasma sintering temperature-pressure profile used to density ThO_2 powders. The maximum temperature was reached at a heating rate of $100^\circ\text{C}/\text{min}$ and maintained for 5 minutes.

Fig. 2

X-ray powder diffraction patterns of ThO_2 and $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$ prior to sintering. The HEBM and $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$ patterns match the commercial ThO_2 pattern with minor lattice contractions. No residue peaks or secondary phases are observable in the $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$ patterns.

Fig. 3

Bright-field TEM imaging of 12 hour HEBM: (A) ThO_2 (B) $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ (C) $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$. Particle sizes range from 10-20 nm for milled powders.

reduced the temperature required to reach full densification as compared to bulk powders. La-content does not appear to significantly affect the SPS densification behavior.

Fig. 5

SEM images of samples sintered at 1600 °C: (A) 12h HEBM ThO_2 (B) 18h HEBM ThO_2 (C) $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ (D) $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ held at 1600 °C for 1h.

Fig. 6

X-ray diffraction results of (A) $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ (B) $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ pellets. The presence of minor La_2O_3 peaks are denoted.

Fig. 7

X-ray diffraction results from 72 to 80 degrees 2θ of (A) $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ (B) $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ pellets. La-rich and La-deficient (ThO_2) phase are denoted. Phase segregation

is visible in both samples starting at 1600 °C, followed by a singular phase, of higher angle for $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$ and lower angle for $\text{Th}_{0.91}\text{La}_{0.09}\text{O}_{1.955}$, at 1700 °C.

Fig. 8

Lattice parameter of sintered pellets: (A) ThO_2 (B) $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$. Minor lattice parameter changes are observed between

milling times in ThO_2 samples. Phase segregation is denoted in $\text{Th}_{1-x}\text{La}_x\text{O}_{2-0.5x}$ by arrows, showing the difference in lattice parameter between the La-rich and La-deficient phases.

Fig. 9

Energy dispersive spectroscopy of $\text{Th}_{0.77}\text{La}_{0.23}\text{O}_{1.885}$ sintered at 1600 $^{\circ}\text{C}$: (A) Back-scattered electron image which shows the presence of a darker secondary phase, (B) EDS spectra of the darker, La-rich phase, (C) EDS spectra of the lighter, La-deficient phase.

Fig. 10

Thermal diffusivity measurements of

(A) ThO₂ (B) Th_{0.91}La_{0.09}O_{1.955} (C) Th_{0.77}La_{0.23}O_{1.885}. Diffusivity beyond 600 °C correlates strongly to the presence of the La-deficient phase.

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